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Carbon Group Chemistry of Humic and Fulvic Acid: A Comparison of C-1s NEXAFS and ^{13}C-NMR Spectroscopies

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Beamline(s): X1A

Introduction: Mobile colloids play an important role in the transport of otherwise relatively immobile, strongly adsorbing contaminants in soils, groundwater aquifers, and fractured rocks (1). Although a range of methods have been applied to characterize colloids and their interaction with contaminants, methods which provide in-situ imaging and spectroscopic characterization are rare. The Scanning Transmission X-ray Microscope (STXM) at X-1A can be used for C-1s Near-Edge X-ray Absorption Fine-Structure (NEXAFS) spectromicroscopy and may therefore provide information on the carbon group chemistry of single colloidal particles. While C-1s NEXAFS spectra of natural organic matter have been interpreted qualitatively in a finger printing approach (2, 3), little is known whether these spectra can be used for a quantitative carbon group analysis comparable to ^{13}C NMR spectroscopy (4).

Methods and Materials: Humic (HA) and fulvic acid (FA) were isolated from a Humic Gleysol in Northern Switzerland and separated into four size fractions using a cross-flow hollow-fibre ultrafiltration technique (5). Solid-state ^{13}C-NMR spectra of the freeze-dried samples were recorded on a Bruker DSX 200 NMR spectrometer at a resonance frequency of 50.3 MHz and with a cross-polarization magic-angle spinning of 6.8 kHz. NEXAFS spectra were collected of thin films of the samples. The spectra were deconvoluted using an arctangent function for the ionization potential (IP) at 290 eV, and 6 Gaussian functions for π* and σ* transitions (4).

Results: The spectra of FA and HA size fractions show three well resolved bands at 285.0, 286.7 and 288.4 eV from aromatic, phenolic and carboxyl groups (Fig. 1). The band areas increase systematically with the relative abundance of the groups as determined by NMR (r = 0.89, 0.91, 0.71). Furthermore, the band areas above the IP representing σ* transitions, correlate with alkyl groups (r=0.71).

Conclusions: Even with a relatively simple fitting approach, quantitative information can be derived from NEXAFS spectra of natural organic matter.

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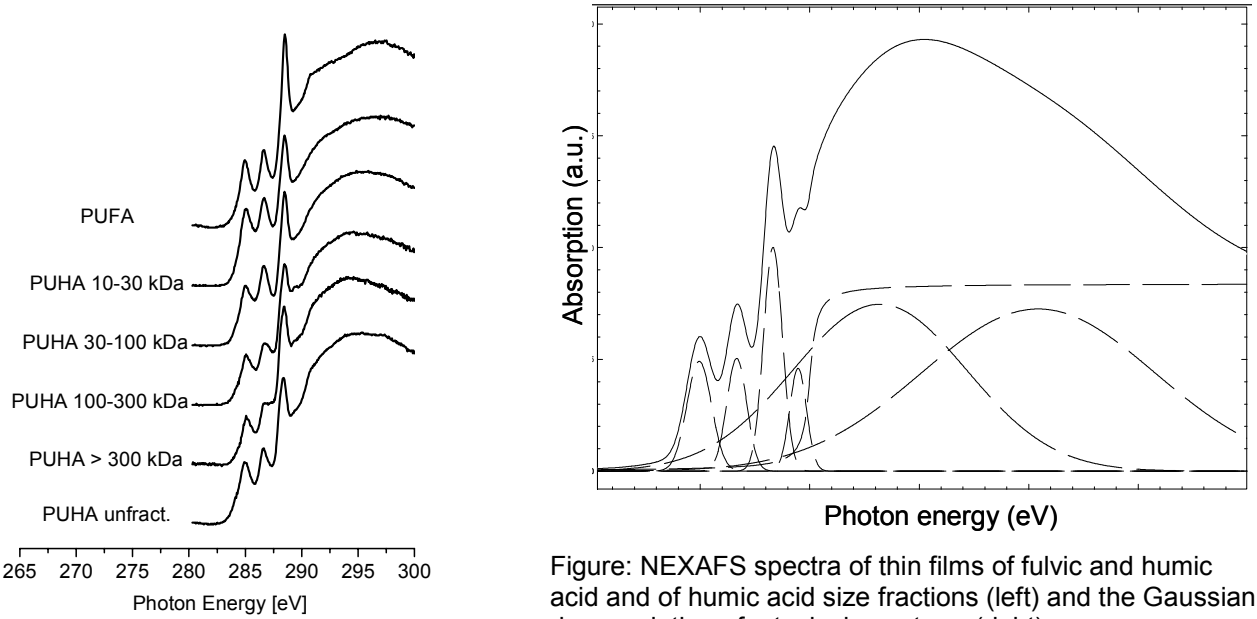

Figure: NEXAFS spectra of thin films of fulvic and humic acid and of humic acid size fractions (left) and the Gaussian deconvolution of a typical spectrum (right).